Calculations of Electric Capacitance in Carbon and BN Nanotubes, and Zigzag Nanographite (BN, BCN) Ribbons

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Abstract

Electronic states in nanographite ribbons with zigzag edges are studied using the extended Hubbard model with nearest neighbor Coulomb interactions. The electronic states with the opposite electric charges separated along both edges are analogous as nanocondensers. Therefore, electric capacitance, defined using a relation of polarizability, is calculated to examine nano-functionalities. We find that the behavior of the capacitance is widely different depending on whether the system is in the magnetic or charge polarized phases. In the magnetic phase, the capacitance is dominated by the presence of the edge states while the ribbon width is small. As the ribbon becomes wider, the capacitance remains with large magnitudes as the system develops into metallic zigzag nanotubes. It is proportional to the inverse of the width, when the system corresponds to the semiconducting nanotubes and the system is in the charge polarized phase also. The latter behavior could be understood by the presence of an energy gap for charge excitations. In the BN (BCN) nanotubes and ribbons, the electronic structure is always like of semiconductors. The calculated capacitance is inversely proportional to the distance between the positive and negative electrodes.

Key words: carbon nanotubes, nanographite, BN (BCN) ribbons, electric capacitance, extended Hubbard model
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1. Introduction

Nano-carbon (C) materials and hetero-materials including borons (B) and nitrogens (N) have been attracting much attention both in the fundamental science and in the interests of application to nanotechnology devices [1,2]. Their physical and chemical natures change variously depending on geometries [1-3]. In carbon nanotubes, diameters and chiral arrangements of hexagonal pattern on tubules decide whether they are metallic or not [1,2].

In nanographites, the edge atoms strongly affect the electronic states [3], and there are nonbonding molecular orbitals localized mainly along the zigzag edges. Recently, we have studied the competition between the spin and charge orderings due to the on-site and nearest neighbor Coulomb interactions [4]. The nearest neighbor Coulomb interaction stabilizes a novel charge polarized (CP) state with a finite electric dipole moment in zigzag ribbons, and it competes with the spin polarized (SP) state. Though it has been discussed that the transverse electric field might induce the first or-

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der phase transition from the SP state to the CP state [4], we need further study in order to reveal what roles such the novel SP and CP states play in actual physical quantities measurable in experiments.

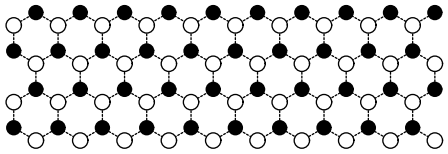

Fig. 1. Schematic structure of the bipartite ribbon with zigzag edges. The filled and open circles are A and B sites, respectively.

2. Carbon nanotubes and nanographite

Figure 1 shows the schematic structure of the nanographite ribbon with zigzag edges. The ribbon is a system with a finite width and an infinite length. Here, we treat the ribbon with a finite width and a finite length, using the periodic boundary condition for the one-dimensional direction. The lattice sites are classified as A and B sites due to the bipartite character. We consider the extended Hubbard model with the inter-site hopping integral t of π-electrons, the onsite U and nearest-neighbor V interactions [4,5]. The typical results will be shown for the representative parameters. Usually, the relation $U > V$ would be satisfied, and the magnitude would be $U \sim$ (a few) eV. The detailed values could be determined by comparing the calculation of the exciton effects with photophysical experiments, for example. The relative stabilities between the CP and SP states have been investigated and summarized in the phase diagram [4]. While U is fairly larger than V, the SP state is more stable. As V becomes stronger, the system exhibits the first order phase transition from the SP state to the CP state. The charge order occurs in the CP phase, while the spin order occurs in the SP phase.

In order to examine nano-functionalities as"nano-size condensers", electric capacitance of the nanographite ribbons is calculated. We assume that the two sets of carbon atoms at the zigzag edges are regarded as positive and negative electrodes, respectively. The spacer between two electrodes is the inner part of the zigzag nanoribbon. The absolute value of the net variation of the accumulated charge is divided by the strength of the small applied voltage, and the capacitance is obtained. We assume that the bond length between carbons is 1.45 Å.

Figure 2 shows the calculated results for the system in the SP state. The actual magnitudes in the logarithmic scale are plotted in Fig. 2 (a) against the ribbon width in the scale of Å, and their inverse values are shown in (b). When the width N of the system increases, it develops into the $(L/2, 0)$ zigzag nanotube due to the periodic boundary condition along the zigzag-edge direction. The nanotube is metallic when $L/2$ is a multiple of three, and is semiconducting for others [2] in the noninteracting model. While the ribbon width is small (approximately $<$ 10 Å), the capacitance would be dominated by the presence of the edge states. Even though the ribbon width becomes larger, the capacitance remains with large magnitudes for $L = 18$, as shown by squares in Fig. 2 (a). This would be related with the resulting metallic properties of the long enough $(9, 0)$ nanotube. On the other hand, the capacitance for $L = 20$ is proportional to the inverse width for larger widths, as shown in Fig. 2 (b). The presence of the semiconducting gap in the $(10, 0)$ nanotube might result in the distinctive difference.

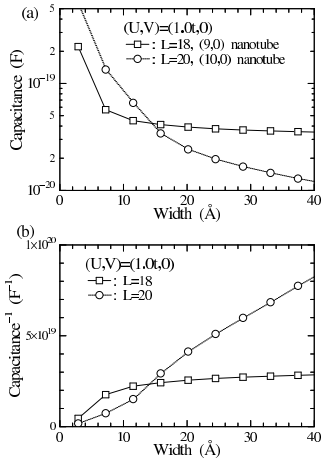

Fig. 2. The electric capacitance calculated for the SP state at $(U, V) = (1.0t, 0)$. Two sets of the ribbon lengths $L = 18$ (squares) and 20 (circles) are considered. The magnitude of the capacitance (a) and its inverse (b) are plotted against the ribbon width in the scale of Å.

Figure 3 summaries the calculated capacitance for

the system in the CP state. The two sets of $L = 18$ and 20 are shown, too. We find that the capacitance is inversely proportional to the graphite width [Fig. 3 (b)]. This behavior does not depend on whether the long enough system is the metallic (9,0) or semiconducting (10,0) nanotube. As the system has the charge orders, electrons would become less mobile than those in the system without ordered states. The behavior could be understood by the presence of an energy gap for charge excitations.

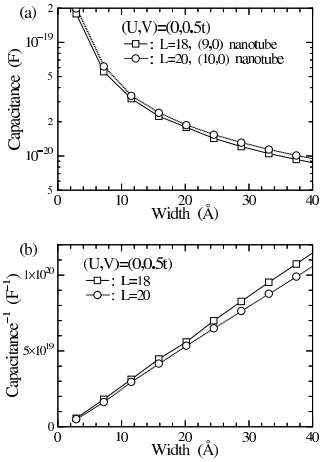

Fig. 3. The electric capacitance calculated for the CP state at $(U, V) = (0, 0.5t)$. Two sets of the ribbon lengths $L = 18$ (squares) and 20 (circles) are considered. The magnitude of the capacitance (a) and its inverse (b) are plotted against the ribbon width in the scale of Å.

The intrinsic capacitance of the single wall carbon nanotube can be estimated as follows. We consider a nanotube with finite length which is present in a quantum box of the length L_y. The wavenumber is quantized with the interval $\Delta k = 2\pi/L_y$. Addition energy of an electron to the nanotube in the quantum box can be equated with an energy as a dielectric system. The addition energy can be estimated to be $\Delta E = (h/2\pi)v_F\Delta k\cdot(1/2)\cdot(1/2)$, where v_F is the Fermi velocity, the first factor (1/2) comes from the degeneracies of spin, and the second one (1/2) is due to the degeneracy of electronic states near the Fermi energy. Here, we assume that the nanotube interacts with circumstances, and the degeneracies of spin and electronic states are lifted slightly. Therefore, ΔE is the overall average level spacing including spin and number of electronic bands. By setting $\Delta E = e^2/2C_QL_y$, we obtain the quantum capacitance per unit length: $C_Q = 2e^2/hv_F$. For carbon nanotubes $v_F = 8 \times 10^5$ (m/s) [6], so that $C_Q = 100$ (aF/μ m) $= 10^{-20}$ (F/Å). In fact, the capacitance per unit length has been measured to be 190 (aF/μ m) [7] for example, and the above rough estimation explains the experimental magnitude fairly well. Such the order of magnitudes of the estimation and experimental value also agrees with that of the capacitance obtained in the calculation within the difference of a few order of magnitudes. Even though the detailed definitions of the capacitances are different mutually, the resulting order of magnitudes should reflect quantum characters of electronic systems.

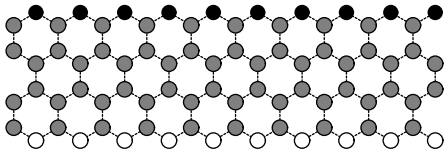

Fig. 4. Schematic structure of the BCN nanoribbon with zigzag edges. The filled, shaded, and open circles are B, C, and N atoms, respectively.

3. BN and BCN systems

We consider hetero-materials composed of B, C, and N. One is the BN ribbon with zigzag edges, and its structure is that of Fig. 1, where B and N atoms exist at the A and B sites, respectively. The other is the BCN system, where one set of edge sites are occupied with B, and another set of edge sites are with N. The inner region of the ribbon is composed of C. The structure is shown in Fig. 4. The experiments of the low concentration limit of B and/or N doping into carbon nanotubes have sometimes suggested accumulation of impurity atoms at edge sites [8]. The formation of zigzag nanotubes is favored. Therefore, we choose this structure as a model system. The site energies at the B and N are taken to be $E_{\rm B} = +t$ and $E_{\rm N} = -t$. The total electron number is same with that of the site number. Such the strong site energy difference gives rise to huge charge polarizations. Therefore, the region of the CP state extends in the phase diagram, and the SP state is highly suppressed. The realistic values of the interactions correspond to CP states in the phase diagram.

In the following, we look at representative behaviors of the electric capacitance of the BN and BCN systems.

Figure 5 shows the electric capacitance of the zigzag BN ribbons with changing the ribbon width. Its raw value (a) and the inverse (b) is plotted. We take three parameter sets of Coulomb interactions. The system is in the CP state for these parameters. Figure 6 shows the calculated results for the BCN system. The system is in the CP state, too. Both calculations show the almost inversely proportional behaviors of the capacitance with respect the ribbon width. There is a huge electronic gap due to the strong site energy difference. The system is a semiconductor intrinsically. The strong charge excitation energy gap results in the inversely proportional behaviors, in contrast to the saturating behaviors of the SP state found for the metallic carbon systems (Fig. 2).

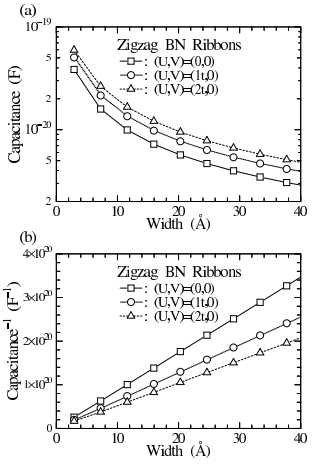

Fig. 5. The electric capacitance calculated for the CP state of the zigzag BN ribbons at $U = 0$, $1t$, and $2t$ with $V = 0$. The ribbon length is $L = 20$. The magnitude of the capacitance (a) and its inverse (b) are plotted against the ribbon width in the scale of Å.

4. Summary

Electric capacitance has been calculated in order to test the nano-functionalities of carbon and BN (BCN) nanotubes and ribbons. In the magnetic phase of the nanographite, as the ribbon becomes wider, the capacitance remains with large magnitudes as the system develops into metallic zigzag nanotubes, while it is proportional to the inverse of the width when the system corresponds to the semiconducting nanotubes. In the charge polarized phase, the capacitance is inversely proportional to the graphite width. In the BN (BCN) nanotubes and ribbons, the electronic structure is always like of semiconductors. The calculated capacitance is inversely proportional to the distance between the positive and negative electrodes.

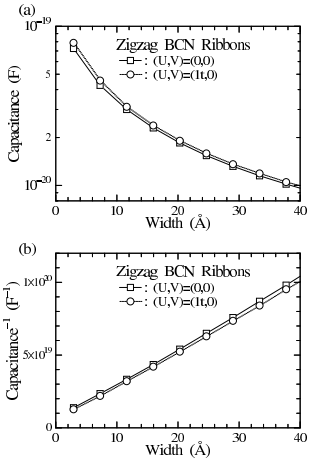

Fig. 6. The electric capacitance calculated for the CP state of the zigzag BCN ribbons at $U = 0$ and $1t$ with $V = 0$. The ribbon length is $L = 20$. The magnitude of the capacitance (a) and its inverse (b) are plotted against the ribbon width in the scale of Å.

References

[1] S. Iijima, Nature **354**, 56 (1991).

[2] R. Saito, G. Dresselhaus, and M. S. Dresselhaus, "Physical Properties of Carbon Nanotubes", (Imperial College Press, London, 1998).

[3] M. Fujita, K. Wakabayashi, K. Nakada, and K. Kusakabe, J. Phys. Soc. Jpn. **65**, 1920 (1996).

[4] A. Yamashiro, Y. Shimoi, K. Harigaya, and K. Wakabayashi, Phys. Rev. B **68**, 193410 (2003).

[5] K. Wakabayashi and K. Harigaya, J. Phys. Soc. Jpn. **72**, 998 (2003).

[6] S. G. Lemay *et al.*, Nature **412**, 617 (2001).

[7] T. Dürkop, S. A. Getty, E. Cobas, and M. S. Fuhrer, Nano Lett. **4**, 35 (2004).

[8] M. Terrones *et al.*, Mater. Today **7** (10), 30 (2004).